

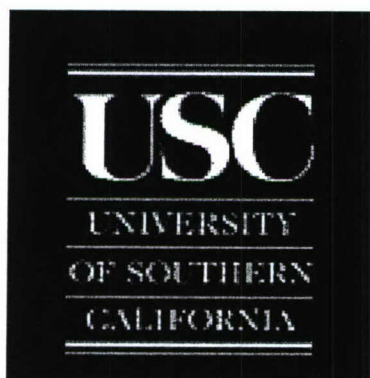
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| 13. ABSTRACT (Maximum 200 Words)<br>The overall objectives of this research are the syntheses and characterization of polynitrogen, high-nitrogen and high-oxygen energetic materials, useful as propellants or explosives ingredients. Excellent results were obtained in all areas and are summarized in 38 publications and 2 patents. The chemistry of $N_5^+$ was developed and 13 new $N_5^+$ salts were prepared and characterized. It was demonstrated that $N_5^+$ cations can be combined with doubly charged anions, thereby doubling the $N_5^+$ content of a salt. Furthermore, it was shown that $N_5^+$ can be combined with highly energetic counter-ions, such as $[B(N_3)_4]^-$ and $[P(N_3)_6]^-$ . Another novel polynitrogen ion, discovered under this program by electrospray ion mass spectroscopy, is the cyclo- $N_5^-$ anion. Two other novel polynitrogen species, the $N_3NOF^+$ and $N_7O^+$ cations, were prepared and characterized. The possible syntheses of compounds, such as $N_5^+N_3^-$ and $N_5^+N_5^-$ , were studied. A new method for the processing of nitrogen NMR data with greatly improved signal to noise ratios was developed and successfully applied to $N_5^+$ . A large number of novel polyazides were prepared and characterized, including: $As(N_3)_3$ , $Sb(N_3)_3$ , $As(N_3)_4^-$ , $As(N_3)_5$ , $Sb(N_3)_5$ , $Sb(N_3)_6^-$ , $P(N_3)_6^-$ , $B(N_3)_4^-$ , $Te(N_3)_4$ , $Te(N_3)_5^-$ , $Te(N_3)_6^{2-}$ , $Ti(N_3)_4$ , $Ti(N_3)_5^-$ , $Ti(N_3)_6^{2-}$ , $W(N_3)_6$ , $W(N_3)_7^-$ , $OW(N_3)_4$ , $OW(N_3)_4 \cdot CH_3CN$ , $OW(N_3)_5^-$ , $Mo(N_3)_6$ , $OMo(N_3)_4^-$ , $Ta(N_3)_5$ , $Ta(N_3)_6^-$ , $Nb(N_3)_5$ , $Nb(N_3)_6^-$ , $Nb(N_3)_5 \cdot NCCCH_3$ , $Te(N_3)_4$ , $Te(N_3)_5^-$ , $Te(N_3)_6^{2-}$ , $U(N_3)_6$ , $[trans-UO_2(N_3)_4]^{2-}$ , $Mn(N_3)_4$ , $[Mn(N_3)_6]^{2-}$ , $[N \equiv W(N_3)_4]^-$ , $[ONb(N_3)_5]^{2-}$ , $[OMo(N_3)_5]^{2-}$ , $[cis-O_2Mo(N_3)_4]^{2-}$ , $[cis-O_2W(N_3)_4]^{2-}$ , $[Ti(N_3)_5OSi(CH_3)_3]^{2-}$ , $V(N_3)_4$ , $V(N_3)_6^-$ , $[V(N_3)_6]^{2-}$ , $[Nb(N_3)_7]^{2-}$ , $[Ta(N_3)_7]^{2-}$ , $[Pd(N_3)_4]^{2-}$ , $[N_5]^+[B(N_3)_4]^-$ , and $[N_5]^+[P(N_3)_6]^-$ . A new concept for liquid monopropellants, based on oxygen-balanced energetic ionic liquids, was developed and successfully demonstrated. A new stable reagent, $NaSO_3NF_2$ , for the introduction of gem-bis $NF_2$ groups was developed. An new solid-gas process, which avoids liquid phase quenching, was invented for generating singlet delta oxygen for the COIL laser. |  |   |  |   |
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# **High Energy Density Material Chemistry**

(F49620-02-1-0229)

## **Final Report**

**May 15, 2002 through October 31, 2006**



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## Objectives

The overall objectives of this research are the syntheses and characterization of polynitrogen, high-nitrogen and high-oxygen energetic materials that are useful as propellants or explosives ingredients.

## Status of Effort

Excellent results were obtained, and significant progress was made towards our objectives, particularly, in the areas of polyazido and polynitrogen chemistry and high-oxygen carriers. Because fluorine compounds play an important role as starting materials in many reactions, some work was also carried out in this area. Completed pieces of work were summarized in manuscript form for publication and are listed under publications. Work in these areas continues at USC under two STTR programs funded by AFOSR.

## Accomplishments

Numerous major breakthroughs were achieved in different areas during this program. The major results in each area are summarized in the following sections.

### A. $N_5^+$ Chemistry

Following our earlier syntheses of  $N_5^+AsF_6^-$  and  $N_5^+SbF_6^-$ , the scope of  $N_5^+$  chemistry was greatly expanded by synthesizing 13 new  $N_5^+$  salts using metathetical approaches [Pubs. 13 and 22]. In connection with this work, we observed that in  $SO_2$  solution,  $SO_2$  interacts with the azide anion. It was found that  $N_3^-$  forms a marginally stable 1:1 adduct with  $SO_2$  and a 1:2 adduct that is stable at lower temperatures [Pubs. 5 and 12]. We have also developed an improved synthesis

for pure  $\text{CsN}_3$  that is based on its adduct formation with  $\text{SO}_2$  [Pub. 2], and a general method for the preparation of anhydrous cesium salts [Pub. 1].

In efforts to synthesize  $\text{N}_5^+$  salts having a higher energy content than  $\text{N}_5^+\text{SbF}_6^-$ , we demonstrated that the energy content can be doubled by doubling the number of  $\text{N}_5^+$  cations per anion. This was achieved by the successful synthesis of  $[\text{N}_5^+]_2[\text{SnF}_6]^{2-}$  [Publ. 13]. This salt decomposes to  $\text{N}_5^+\text{SnF}_5^-$  and one equivalent of  $\text{FN}_5$ . Because our experimental efforts to trap  $\text{FN}_5$  were unsuccessful, a theoretical study of the stability of  $\text{FN}_5$  was carried out. It was found that the predicted life time of  $\text{FN}_5$  is so short that it precludes its observation [Publ. 15]. As a next step, we studied, both experimentally and computationally, the possibility of combining the  $\text{N}_5^+$  cation with highly energetic anions, such as  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{N}_3^-$  or  $\text{N}_5^-$ . It was found that all these anions cannot form stable salts with  $\text{N}_5^+$  [Publ. 18]. However, we have succeeded to isolate and characterize with  $[\text{N}_5]^+[\text{B}(\text{N}_3)_4]^-$  and  $[\text{N}_5]^+[\text{P}(\text{N}_3)_6]^-$  two extremely energetic salts [Publ. 22]. Although these salts are much too sensitive for practical use and explode violently upon warm up to room temperature, they nevertheless demonstrate the principle that  $\text{N}_5^+$  can indeed be combined with highly energetic anions.

We have also developed a more powerful  $^{15}\text{N}$  NMR method for the characterization of polynitrogen compounds which does not require time consuming and expensive enrichment procedures. This new technique was demonstrated for  $\text{N}_5^+$  and allowed us to observe all its NMR parameters in natural abundance [Publ. 31].

## B. $\text{N}_5^-$ Chemistry

Another important discovery was the experimental detection of the pentazolate anion, *cyclo*- $\text{N}_5^-$  by electrospray ion mass spectroscopy. It was published as a hot paper in *Angewandte Chemie* [Publ. 6] and highlighted in *Chemical & Engineering News*.

In pursuit of a bulk synthesis for  $N_5^-$ , the possibility of preparing trialkylsilyldiazonium salts was explored because their Si-N bonds might be cleaved readily by strong nucleophiles. Numerous reactions were investigated, but were unsuccessful. Theoretical calculations on the stability of trialkylsilyldiazonium salts confirmed that, in accord with our experimental findings, these compounds spontaneously lose  $N_2$ . These calculations also showed that replacement of the trialkyl groups by perfluorotrialkyl groups could lead to stable products.

During our search for alkyl diazonium salts, a potential starting material, the new compound  $(C_6H_5)_3CNSO$ , was prepared and characterized [Publ. 7]. Also, dimethylamino substituted arylpentazole was prepared and its decomposition in different solvents was studied, but no selective cleavage of the *ipso*-C-N bond was observed with conservation of the  $N_5$  ring.

In a paper following our original report on  $N_5^-$  [Publ. 6], Butler from Ireland reported, based on NMR observations, a bulk synthesis for this ion. Because we had strong reservations about the validity of his claim, we have repeated his work using isotopic substitution experiments. We were able to show conclusively that Butler had misinterpreted his results and that the resonance attributed by him to  $N_5^-$  is actually due to the  $NO_3^-$  anion [Publ. 26].

### C. Polyazides

In the area of polyazido compounds, impressive progress was made. The following novel compounds were prepared and characterized by vibrational spectroscopy, theoretical calculations, and in many cases by their crystal structures:  $As(N_3)_3$ ,  $Sb(N_3)_3$ ,  $As(N_3)_4^-$ ,  $As(N_3)_5$ ,  $Sb(N_3)_5$ ,  $Sb(N_3)_6^-$ ,  $P(N_3)_6^-$ ,  $B(N_3)_4^-$ ,  $Te(N_3)_4$ ,  $Te(N_3)_5^-$ ,  $Te(N_3)_6^{2-}$ ,  $Ti(N_3)_4$ ,  $Ti(N_3)_5^-$ ,  $Ti(N_3)_6^{2-}$ ,  $W(N_3)_6$ ,  $W(N_3)_7^-$ ,  $OW(N_3)_4$ ,  $OW(N_3)_4 \cdot CH_3CN$ ,  $OW(N_3)_5^-$ ,  $Mo(N_3)_6$ ,  $OMo(N_3)_4^-$ ,  $Ta(N_3)_5$ ,  $Ta(N_3)_6^-$ ,  $Nb(N_3)_5$ ,  $Nb(N_3)_6^-$ ,  $Nb(N_3)_5 \cdot NCCH_3$ ,  $Te(N_3)_4$ ,  $Te(N_3)_5^-$ ,  $Te(N_3)_6^{2-}$ ,  $U(N_3)_6$ ,  $[trans-UO_2(N_3)_4]^{2-}$ ,  $Mn(N_3)_4$ ,  $[Mn(N_3)_6]^{2-}$ ,  $[N \equiv W(N_3)_4]^-$ ,  $[ONb(N_3)_5]^{2-}$ ,  $[OMo(N_3)_5]^{2-}$ ,  $[cis-O_2Mo(N_3)_4]^2$ ,  $[cis-$



$\text{O}_2\text{W}(\text{N}_3)_4]^{2-}$ ,  $[\text{Ti}(\text{N}_3)_5\text{OSi}(\text{CH}_3)_3]^{2-}$ ,  $\text{V}(\text{N}_3)_4$ ,  $\text{V}(\text{N}_3)_6^-$ ,  $[\text{V}(\text{N}_3)_6]^{2-}$ ,  $[\text{Nb}(\text{N}_3)_7]^{2-}$ ,  $[\text{Ta}(\text{N}_3)_7]^{2-}$ ,  $[\text{Pd}(\text{N}_3)_4]^{2-}$ ,  $[\text{N}_5]^+[\text{B}(\text{N}_3)_4]^-$ , and  $[\text{N}_5]^+[\text{P}(\text{N}_3)_6]^-$ . Most of these compounds are very powerful explosives, and in many instances, previous investigators have not been able to either handle or characterize these compounds. Only a small portion of this work has been published so far [Publs. 19, 20, 24, 25, 28, 32, 37], and numerous manuscripts still need to be written in this area. Several of our publications in this area have received wide public attention. Two papers on tellurium azides and titanium azides, which were published in *Angewandte Chemie*, were highlighted in *Chemical and Engineering News*. Our paper on arsenic and antimony triazides made the cover page of *Chemistry – A European Journal*.  $\text{Nb}(\text{N}_3)_5\cdot\text{NCCH}_3$  is also of special interest because it represents the first example of a compound with a linear metal-N-N bond. Also, the transition from ionic to covalent azides with increasing coordination number of the central atom within the same group of the periodic system was demonstrated for the  $\text{MPh}_4\text{N}_3$  series,  $\text{PPh}_4\text{N}_3$ ,  $\text{AsPh}_4\text{N}_3$ , and  $\text{SbPh}_4\text{N}_3$  [Publ. 29].

#### D. Azidamines

We were also actively studying the conversion of nitrogen chlorides into nitrogen azides as a potential synthesis for novel polynitrogens, such as  $\text{N}(\text{N}_3)_2^-$  or  $\text{N}(\text{N}_3)_3$ . To this end, we have synthesized some novel and some previously reported but ill characterized  $\text{R}_3\text{SiNCl}_2$  compounds. [Publ. 38]. However, these compounds were highly unreactive toward azide ion and did not yield any azidamines. Some forty years ago, Bock and Kompa reported the synthesis of  $(\text{CH}_3)_2\text{N}-\text{N}_3$ , however the compound was not properly characterized. We have repeated this synthesis under similar conditions and found that this reaction is much more complex than previously reported. Particularly, there is a competing side reaction between azide ion and the  $\text{CH}_2\text{Cl}_2$  solvent going on that yields covalent azidomethanes which was not recognized by Bock and Kompa. The

(Me<sub>3</sub>Si)<sub>2</sub>NCl molecule also did not undergo Cl – azide ligand exchange, but with HF, the novel NH<sub>3</sub>Cl<sup>+</sup> cation was obtained and characterized [Publ. 23].

### E. Novel Polynitrogens

We have continued to pursue the synthesis of the N<sub>3</sub><sup>+</sup> cation by studying the possibility of abstracting a fluoride anion from FN<sub>3</sub> using a strong Lewis acid, such as SbF<sub>5</sub>. Because no convenient synthesis for the highly shock-sensitive FN<sub>3</sub> was known, we first had to develop a convenient, high-yield synthesis of pure FN<sub>3</sub>. This was achieved by using either HN<sub>3</sub> or (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub> and elemental fluorine in a suitable solvent. We then studied the reaction of FN<sub>3</sub> with SbF<sub>5</sub> in these solutions and characterized the resulting product. It was shown that FN<sub>3</sub> and SbF<sub>5</sub> form indeed a 1:1 adduct, however, this adduct involves an N-Sb bridge and not an F-Sb bridge. This result was also confirmed by theoretical calculations which showed that the alpha nitrogen atom of FN<sub>3</sub> is a better electron density donor than fluorine. Decomposition of this 1:1 adduct in HF resulted in the formation of the NH<sub>2</sub>F<sub>2</sub><sup>+</sup> cation and allowed us to determine its crystal structure,

We have also pursued the syntheses of the N<sub>3</sub>NOF<sup>+</sup> and N<sub>7</sub>O<sup>+</sup> cations. It was found that ONF<sub>2</sub><sup>+</sup> salts react with either HN<sub>3</sub> or (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub> to give the novel N<sub>3</sub>NOF<sup>+</sup> cation. This cation was isolated in the form of its SbF<sub>6</sub><sup>-</sup> salt and characterized by vibrational and multinuclear NMR spectroscopy and theoretical calculations. It is formed either as a *z*- or *e*-isomer depending on whether the N<sub>3</sub> ligand is *cis* or *trans* with respect to the fluorine ligand.

The replacement of the second fluorine ligand of ONF<sub>2</sub><sup>+</sup> by azide resulted in the formation of the N<sub>7</sub>O<sup>+</sup> cation. However, this cation readily loses one mol of N<sub>2</sub>O giving N<sub>5</sub><sup>+</sup> salts.



## F. Fluorine Chemistry

Fluorine compounds play an important role not only as energetic materials, but also as highly reactive starting materials and reagents. For example, our studies were successful to find a stable, storable and readily preparable  $\text{HNF}_2$  source for the synthesis of *gem*-bis- $\text{NF}_2$  substituted high energy propellants and explosives, such as the *gem*-bis(difluoramine) substituted cyclic nitramines,  $\text{HNF}_2$  and  $\text{TNF}_2$ . It was shown that the direct fluorination of the  $\text{Na}^+\text{SO}_3\text{NH}_2^-$  anion with  $\text{F}_2$  produces  $\text{Na}^+\text{SO}_3\text{NF}_2^-$  in high yield. This salt was characterized by spectroscopy and its crystal structure and, when reacted with carbonyl groups in conc. sulfuric acid, it can replace the oxygen atom by two  $\text{NF}_2$  groups [Publ. 33].

We have also solved a long-standing problem in  $\text{NF}_4^+$  chemistry. The reported vibrational and NMR spectra suggested the presence of perfectly tetrahedral ions while a crystal structure showed two kind of strongly distorted ions. It was shown that the previous crystal structure was flawed by disorder and that the  $\text{NF}_4^+$  cations are indeed tetrahedral [Publ. 34].

$\text{ClF}_3\text{O}$  is the highest performing earth-storable liquid oxidizer for rocket propulsion. We have written up the results of a previous Rocketdyne study on the kinetics of the  $\text{ClF}_3\text{O}$  formation for publication in a memorial issue for the 100<sup>th</sup> birthday of Prof. Schuhmacher who has pioneered this area of research [Publ. 30].

We have also published papers on the structures of  $\text{BrF}_4^+$  and  $\text{ClF}_4^+$  [Publ. 8],  $\text{ClF}_3\text{O}$  [Publ. 11],  $\text{IO}_2\text{F}_5^{2-}$  [Publ. 14],  $\text{ClF}_6^+$  [Publ. 21] and  $\text{XeF}_6$  [Publ. 27], and on the nakedness of the fluoride anion [Publ. 16 and 17].

## G. Chemical Oxygen Iodine Laser

In support of the chemical oxygen iodine laser program of the Air Force, we have developed a new gas-solid method for the generation of singlet delta oxygen which avoids the liquid phase



quenching problems encountered with the wet basic hydrogen peroxide chlorine process [Publ.9 and Pat. 1].

#### **H. High-Oxygen Carriers and Ionic Liquid Based Liquid Monopropellants**

The presently used state of the art monopropellant is hydrazine. Its performance is poor and it is a carcinogen possessing relatively high vapor toxicity. This problem was overcome by developing a new concept [Pat. 2] of using oxidizer balanced, energetic, ionic liquids. The major problem was to provide sufficient oxygen for complete oxidation of the relatively large organic cations. Using large complex inorganic cations, such as tetranitrato borates or aluminates, and more energetic cations, such as tetrazolium salts, high performing liquid nontoxic monopropellants were prepared [Publ. 36].

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(35) “Following in the Footsteps of Henri Moissan,” L’Actualite Chimique, Oct/Nov Issue, 2006, K. O. Christe.

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## **Interactions/Transitions**

### **Presentations:**

52 invited lectures were presented on results obtained under this program at international and national conferences and universities.

2002 AFOSR Molecular Dynamics Conference, Waltham, MA

2002 Gordon Research Conference on Energetic Materials, Tilton, NH

2002 ACS National Meeting, Boston, MA

Invited Seminars at Harvard University / MIT / USC

2002 Geoffrey Coates Lecture, University of Wyoming, Laramie, WY

2002 HEDM/NANO Conference, Washington, DC

2002 Advanced Energetics Technology Exchange Meeting, Livermore, CA

2003 ACS Winter Fluorine Conference, St. Pete Beach, FL (2 papers)

2003 National ACS Meeting, New Orleans, LA (7 papers)

Invited Seminars, UC San Diego and McMaster University, Hamilton, Ontario

2003 Samuel M. McElvain Lecture, University of Wisconsin, Madison,

2003 ACS Inorganic Chemistry Award Lecture, Northwestern University

2003 AFOSR Molecular Dynamics Conference, San Diego, CA

2003 National ACS Meeting, New York, NY

2003 Advanced Energetics Technology Exchange Meeting, Aberdeen, NJ

2004 National ACS Meeting, Anaheim, CA

2004 Science Advisory Board, Wright Patterson AFB, Dayton, OH

2004 European Symposium on Fluorine Chemistry, Poznan, Poland (2 papers)

Invited Seminar, University of Alberta, Edmonton, AL, Canada

10<sup>th</sup> Olah Nobel Prize Symposium, University of Southern California, Los Angeles, CA

2004 Molecular Dynamics Conference, Newport, RI

2004 Winter Symposium, University of Helsinki, Finland

2005 ACS Winter Fluorine Conference, St. Pete Beach, FL, (2 papers)

2005 Energetic Materials Technology Exchange, Washington, DC

2005 National ACS Meeting, San Diego, CA

2005 Molecular Dynamics Conference, Monterey, CA

2005 International Fluorine Symposium, Shanghai, China

Invited Seminar, Lawrence Livermore National Laboratory, Livermore, CA

2005 Pacific Basin Countries Conference, Honolulu, HI (3 papers)



2006 AFOSR Workshop on Ionic Liquids, University of Alabama, Tuscaloosa

2006 Molecular Dynamics Conference, Arlington, VA

Invited Seminars, Los Alamos National Laboratory, Los Alamos, NM, and University of Lethbridge, Lethbridge, Canada

2006 National ACS Meeting, Atlanta, GA

2006 Pyrotechnics Workshop, Fort Collins, CO

2006 International Fluorine Symposium, Bremen, Germany (2 papers)

2006 AFOSR Workshop on Polynitrogen Chemistry, Los Angeles, CA

2006 William Weber Symposium, USC, Los Angeles, CA

### **Joint projects**

Joint projects were carried out with the following groups and colleagues:

Dr. Boatz, AFRL Edwards

Prof. Schrobilgen, McMaster University, Canada

Prof. Dixon, University of Alabama, Tuscaloosa

Dr. Feller, Pacific Northwest National Laboratory

Prof. Gordon, Iowa State University

Prof. Klapoetke, University of Munich, Germany

Prof. Jenkins, University of Warwick, UK

Profs. Prakash and Olah, University of Southern California

Dr. Hemley, Carnegie Institution

Prof. Bau, University of Southern California

Dr. Jurek Krzystek, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL

Prof. Joshua Telser, Roosevelt University, ILL

Dr. Robert Chapman, Naval Research Laboratory, China Lake, CA

Prof. Howard Taylor, University of Southern California

Prof. Konrad Seppelt, Free University, Berlin, Germany

### **Consulting activities**

Consultations were provided to the US Enrichment Corporation of Piketon, OH, in support of their efforts to safely decommission the old gaseous diffusion plants in the US, the Merck GMBH in Darmstadt Germany, the Edwards AFB, and Science and Application Technologies in Moorpark, CA.

### **Patents**

- (1) "Process for the Chemical Generation of Singlet Delta Oxygen," U.S.\_6,623,718 (2002), K. O. Christe and A. Alfano.
- (2) "Novel Liquid Monopropellants," U. S. Patent pending, K. O. Christe and G. Drake.

### **Honors / Awards**

2002 Geoffrey Coates Lecturer, University of Wyoming, Laramie

2003 ACS Award in Inorganic Chemistry

2003 Samuel M. McElvain Lecturer, University of Wisconsin, Madison

2003 ACS Inorganic Chemistry Award Lecturer, Northwestern University

2006 Alfred Stock Memorial Prize from the German Chemical Society

### **Prior Major Awards**

1969 NASA Apollo Achievement Award

1986 ACS Award for Creative Work in Fluorine Chemistry

2000 Prix Moissan

**The full text of all publications has been attached as a separate file.**